PROCESS FOR MAKING THERMALLY STABLE METAL COATED POLYMERIC MONOFILAMENT OR YARN

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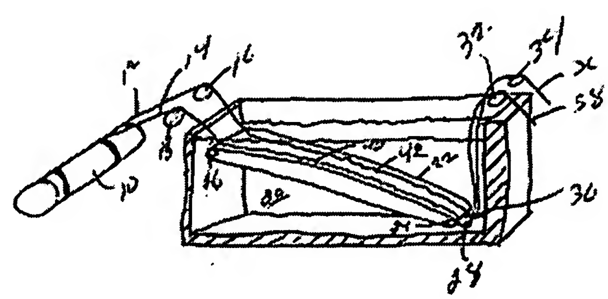
Abstract of **WO9748832**

Monofilaments of a yarn to be coated with electroless nickel are pretreated with an acid and a surfactant to render the monofilament surfaces water wettable and not substantially mechanically degraded. The pretreated yarns is passed through an electroless nickel coating bath under little or no tension so that the electroless nickel can coat all of the monofilament surfaces substantially uniformly. The nickel coated yarn then can be coated with electrolytic metal such as copper in an electrolytic metal plating step, as desired.



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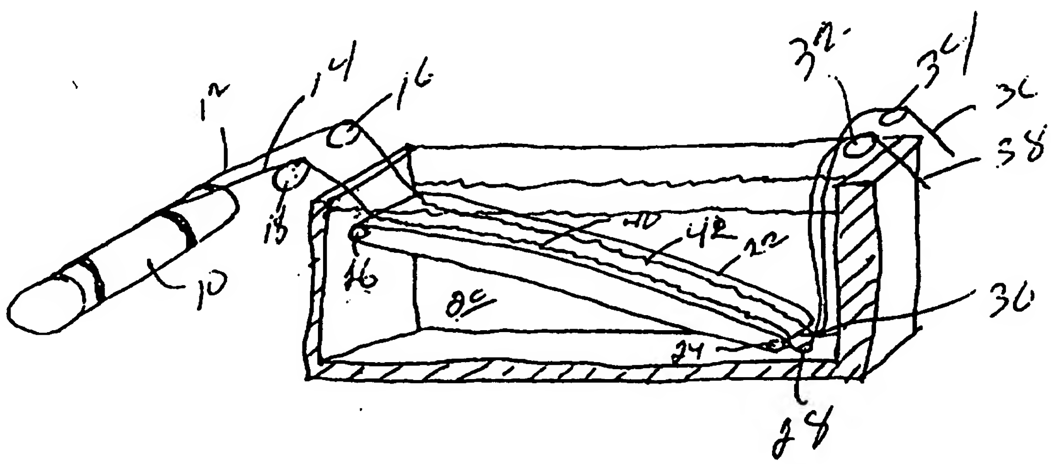

(57) Abstract

Monofilaments of a yarn to be coated with electroless nickel are pretreated with an acid and a surfactant to render the monofilament surfaces water wettable and not substantially mechanically degraded. The pretreated yarns is passed through an electroless nickel coating bath under little or no tension so that the electroless nickel can coat all of the monofilament surfaces substantially uniformly. The nickel coated yarn then can be coated with electrolytic metal such as copper in an electrolytic metal plating step, as desired.

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TITLE

Process for Making Thermally Stable Metal Coated Polymeric Monofilament or Yarn

This invention relates to a process for making completely and substantially uniformly metal coated polymeric monofilaments or yarn made from a plurality of such polymeric monofilaments which are coated with electrolessly deposited nickel and optionally with electrolytically deposited metal on the nickel. More particularly, this invention relates to a process for activating the surfaces of polymeric monofilaments which are subsequently coated with electrolessly deposited nickel.

Up to the time of this invention, it was difficult to deposit metal coatings onto polymeric monofilaments or multifilament yarns to form composite products which were thermally stable and/or to deposit metal coatings which were not easily removed from the monofilament or yarn by low or moderate frictional forces. It has been proposed to coat polymeric fibers with electrolessly deposited copper followed by electrolytically deposited copper. When subjected to thermal cycling tests, however, these coatings are unstable in that they crack and lose metal adhesion.

In order to provide a commercially viable process for metal coating yarns, a continuous process rather then a batch process must be provided. In such a process, yarn of monofilaments to be treated is unwound from a feed storage reel, passed through the appropriate chemical treating steps and then stored on a take up reel. Unfortunately, in presently available yarn processing means, the monofilaments positioned within the interior of the yarn are not coated or are insufficiently coated so that the metal coatings on the monofilaments are non-uniform. A non-uniformly coated yarn has undesirable nonuniform electrical conductivity. In many applications, such as for protective outside layers for cables, non-uniform metal outside layers are unacceptable.

It has been extremely difficult to deposit electroless nickel uniformly and completely onto the surface of monofilaments in a multifilament yarn bundle by wet chemical electroless processes. Various types of pre-woven fabric are coated with electroless metal, primarily electroless copper, for use as electromagnetic interference (EMI) control and shielding. However, electroless copper, although appearing to have adequate adhesion to the individual monofilament polymer surface in a pre-woven

fabric, for reasons not entirely understood, will not maintain its adhesion after exposure to high temperature or humidity exposure. This problem can be alleviated by using electroless nickel which forms tight polymeric bonds to the various functional groups on the surface of polymers which have been treated by the process of this invention. The resultant nickel-coated filaments are resistant to degradation exposure to thermal cycling and humidity.

In a process for depositing electroless metal in a polymeric surface, it is generally necessary to treat the surface so that it will accept a catalyst for the electroless metal deposition. U.S. Patent 5,302,415 describes a process for electrolessly metalizing various aramid fibers using copper, nickel, silver, or cobalt. The disclosed process utilizes an 80 to 90% sulfuric acid solution to modify the surfaces of the aramid fibers. Modification is achieved by controlled fiber degradation as a consequence of depolymerization, to provide sites for the deposition of a sensitizer which promotes electroless metal deposition. However, the aramid fibers cannot be contacted with this strong sulfuric acid solution for more than a short time period because the fibers will dissolve or be degraded in the acid. The deposition of electroless copper typically produces a coarse-grained coating which lacks the adhesion, ductility and flexural endurance that cable shielding applications in question require. Furthermore, an all-electroless copper construction requires the addition of another metal layer on each monofilament to protect the exposed copper against long-term oxidation. Nickel deposition by conventional phosphite-reduced electroless nickel processes results in a coating with a conductivity typically less than 15% that of copper. Due to oxidation of the phosphorous in the nickel-phosphorous alloy, of those nickel processes, such coatings form a much more stable surface and are generally preferred for applications involving high corrosion resistance. However, they are highly resistive and difficult to clean. For that reason, it is difficult to electroplate other metals on these nickel-phosphorous layers, especially when the surface to be coated is on polymeric filaments. Thus, an all-electroless nickel based on conventional phosphite-reduced chemistry is poorly-suited to the goal of achieving a metalized fiber coating with a high conductivity to weight/thickness aspect.

Accordingly it would be desirable to provide a process for making polymeric yarn which is completely and substantially uniformly coated with a metal. It would also be desirable to provide such a completely coated yarn capable of having a high conductivity to weight/thickness aspect. In addition, it would be desirable to provide such a process including a polymer surface

activation step which does not substantially degrade the polymeric monofilament or yarn. In addition it would be desirable to provide such a metal coated yarn which can be formed by continuous reel-to-reel process. Such a process would permit the commercial production of completely and substantially uniformly metal coated yarn that could be utilized in a wide variety of environments such as EMI shielding.

SUMMARY OF THE INVENTION

The present invention provides a process for modifying the surface of a polymeric monofilament to render said surface water-wettable characterized by contacting said surface with an aqueous activating solution comprising sulfuric acid or a strong acid derivative of sulfuric acid having a concentration of 75 to 85 percent by weight and a surfactant for a time period and temperature sufficient to render said surfaces water-wettable but less than that wherein substantial mechanical degradation of said monofilament occurs.

The present invention also provides a process for completely and substantially uniformly coating the surface of a polymeric monofilament with an electrically conductive electroless nickel coating wherein said surface is modified by the process of contacting the monofilament with acid and surfactant solution prior to coating with said nickel characterized by feeding said monofilament from at least one feed reel, through an electroless nickel bath to at least one take-up reel wherein tension on said monofilament within said bath is sufficiently low to permit complete and substantially uniform coating.

The invention includes monofilaments and yarns of monofilaments coated with electrically conductive nickel-boron alloy coatings.

BRIEF DESCRIPTION OF THE DRAWING

The figure shows an apparatus suitable for processing yarn in accordance with this invention.

DETAILED DESCRIPTION OF THE INVENTION

As a first step, in accordance with practice of the process of this invention, the surfaces of monofilaments in a yarn to be coated with metal are contacted with an aqueous activating solution which renders the surfaces hydrophilic and facilitates adsorption of a catalyst for effecting electroless nickel deposition. The aqueous activating solution comprises an acid such as

sulfuric acid, or a strong acid derivative of sulfuric acid such as methane-sulfonic acid, chlorosulfonic acid, fluorosulfonic acid, and the like and a surfactant having from 8 to 12 carbon atoms. Suitable surfactants include fluoroalkyl salts, ethers and esters, polyethoxylated quaternary ammonium salts, sodium alkyl benzoates, polyethoxylated straight chain alcohols and the like. Particularly suitable surfactants include amine perflouroralkyl sulfonates, fluorinated alkyl alkoxylates, fluorinated alkylesters, fluorinated alkyl carboxylate salts or the like. The use of the surfactant permits using weaker acid compositions which permits longer contact times with the monofilament without substantial degradation. The increased permissible contact times permit increased penetration of the aqueous activating composition into interior monofilaments of any yarn being treated.

The yarn or monofilament surfaces then are contacted with a palladium catalyst in order to provide a catalytic surface for the electroless deposition of electrically conductive metal. As used herein, the term "nickel" as it relates to the electrolessly-applied metal coating, refers to a nickel/boron alloy and excludes nickel/phosphorous alloys. The electroless nickel bath contains both nickel and boron and a reducing agent which produces the nickel-boron alloy coating for the polymeric monofilaments.

After the activating solution contact step, monofilaments to be metal coated are passed, generally as yarn, through an electroless bath to coat nickel completely and substantially uniformly on all the monofilament surfaces. Tension on the yarn passing through the electroless nickel bath is either eliminated or maintained sufficiently low so that the nickel coatingsolution can penetrate into and through the entire yarn bundle, in particular even on the surface of monofilaments located within the yarn bundle interior. It has been found that when the yarn is passed through the electroless nickel bath under moderate significant tension, , the monofilaments at the interior of the yarn bundle are either not coated at all or are incompletely coated so that the metal coating on the monofilaments is not uniform.

After the electroless nickel coating of this invention,, the nickel coated yarn can be coated electrolytically with an electrolytic metal such as copper or nickel. The electrolytic metal deposition also can be effected in a reel to reel process wherein the nickel-coated yarn positioned within an agitated electrolytic aqueous bath is subjected to little or no tension to permit the aqueous electrolytic bath to penetrate into the interior of the yarn to be coated.

When utilizing polyaramid monofilament as the polymeric monofilament or yarn, an optimal composite for electronic shielding and signal-carrying applications where the combination of low electrical resistance and high strength-to-weight is an important design objective is obtained. The nickel coated or nickel and electrolytic metal coated monofilament or yarn, which can be braided or woven, functions as a substitute for metal wire. The multilayer structure, as well as the process for producing it, embody several improvements over the prior art, among them:

1. The use of an amine-borane reduced electroless nickel as the initial metalization layer to achieve:

(a) a metal-polymer bond that in conjunction with a suitably treated polymer surface, does not noticeably degrade under exposure to temperature/humidity cycling or soldering temperatures;

(b) a virtually pure nickel substrate

(1) is metallurgically compatible with a subsequent electrolytically applied layer of metal such as copper,

(2) inhibits the migration of absorbed moisture or oxygen from the polymer at the interface between the nickel layer and the metal e.g. copper layer,

(3) is sufficiently conductive in thin layers (less than 0.5 micron thick) to enable the metal, e.g. copper to be deposited by high speed electroplating;

(c) uniform and complete metalization of each monofilament in the polymeric yarn bundle.

2. A layer of electrolytically-deposited metal, e.g. copper over the amine-borane nickel layer that, by reason of its dense fine-grained composition, (a) has excellent ductility and flexural endurance properties; (b) is more conductive per unit weight than electroless copper.

3. One or more electrolytically-deposited layers of nickel, silver, tin, etc., over the copper layer to provide oxidation/corrosion protection as well as abrasion resistance to the copper.

In one embodiment of a utility of this invention, a construction is provided consisting of a yarn bundle of polyaramid monofilaments metalized with amine-borane reduced electroless nickel only. When chopped into short lengths, such metalized fibers find utility as conductive fillers which minimize electrostatic buildup on the surface of molded plastic parts used in electrical/electronic applications. In this embodiment the idealized metal coating must be bonded to the polyaramid monofilament surfaces with

sufficient adhesion to withstand the mechanical abrasion of the chopping as well as the elevated temperature experienced in the injection molding processes, while at the same time providing an acceptable level of conductivity which does not materially change due to oxidation, unlike nickel-phosphorous alloy in the 10-20 ohm/foot range.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The monofilament surfaces to be treated in accordance with this invention are formed from a polymeric compositions rendered more hydrophilic by the acid and surfactant activating solution to enable a more complete and more uniform electroless nickel coating on all the monofilament surfaces which is adherent and sufficiently electrically conductive to facilitate subsequent electrolytic metal coating on the conductive nickel. Representative suitable polymeric compositions for forming the monofilament or yarn include aramid, such as poly(p-phenylene terephthalamide), poly (m-phenylene isophthalamide), and the like, polyamide, such as nylon 6, nylon 66, and the like, polyester, polyimide, polyetherimide, acrylics, polytetrafluoroethylene and the like, preferably aramid since it provides excellent tensile strength per unit weight. Typically yarns have a denier between about 55 and 3,000 and more typically between about 55 and 600 with 10-15 micron diameter monofilaments. The monofilaments can be solid or hollow.

It has been found that more effective penetration of acid into the yarn is obtained with surfactant in the acid than with an unadulterated acid solution. A surfactant permits using a weaker acid which results in reduced degradation to the monofilament surfaces. In the case of sulfuric acid used in combination with a surfactant, 75 to 85%, preferably 78 to 83% sulfuric acid can be utilized which permits increasing the contact time of the yarn with the activating composition considerably while avoiding undesirable monofilament degradation. The increased contact time and the presence of a surfactant provides more complete penetration of the activating solution into the yarn and thereby permits greater assurance of subsequent complete and substantially uniform electroless metal coating. The surfactant is utilized in concentration between about 10 and 1000 parts per million (ppm) preferably between about 100 and 500 ppm of the activating solution.

While the use of surfactant in the activating solution is preferred and produces a surprisingly improved product, acceptable nickel coated monofilaments can be made by treating the monofilaments with solutions

known to improve the water wettability of surfaces such as potassium hydroxide, sodium hydroxide, or other caustic compositions used alone or in combination with a lower alcohol such methanol or ethanol, or chromic acid, or the like. The monofilaments can, also, be treated by immersion in concentrated sulfuric acid as described in U.S. Patent 5,302,415, such as, for example, by immersion in 80 to 90 weight percent sulfuric acid, for 2 to 60 seconds at 10 to 100°C, although the fibers may be somewhat degraded by such immersion.

Once the monofilament surfaces have been rendered water wettable, the surfaces are contacted with any one of the catalyst systems well known to those versed in the art of electroless plating to effect electroless metal deposition. Catalyst combinations which can be used in conjunction with the sensitized surfaces are disclosed in U.S. Pat. Nos. 3,011,920 and 3,562,038. The catalyst application is provided for a period, generally of one to about five minutes, and then the sample is immersed in an acidic solution to remove tin from the surface in the process referred to as acceleration. The sample is then passed through in an electroless nickel bath for a period ranging from about two to ten minutes to provide the desired thickness of nickel.

Deposition and activation of the catalyst and subsequent deposition of the electroless nickel is conducted with the yarn under tension which is zero or is sufficiently low so that the treatment baths contact all the monofilament surfaces.

Referring to the figure, a storage roll 10 has wound upon it multifilament yarns, 12 and 14. Guide rollers 16 and 18 pull yarns 14 and 12 from storage roll 10 and deposit the yarns within bath 20 and onto endless web 22. Endless web 22 is moved about rollers 24 and 26, at least one of which is powered. Yarns 12 and 14 are passed under guide rollers 28 and 30 and are removed from bath 20 by powered rollers 32 and 34 as treated yarn 36 and 38. The bath can be the pretreatment bath, the catalyst deposition or activation bath or the electroless nickel bath described above. Powered rollers 32 and 34 and the endless web 22 are operated at a speed to assure little or no tension on the yarns 40 and 42 deposited in the bath 20 on endless web 22. Thus, the entire surface of each monofilament in the yarns is contacted with the composition of bath 20.

Suitable electroless nickel baths are those which are boron-based rather than phosphorous based since the boron based baths deposit a form of nickel resistant to oxidation and which are sufficiently conductive to facilitate subsequent electrolytic metal deposition, such as copper onto the nickel

surface. Suitable boron based electroless nickel baths are disclosed in U.S. Pat. Nos. 3,062,666; 3,140,188; 3,338,762; 3,531,301; 3,537,878; and 3,562,038. Some typical formulations are as follow:

1.	Nickel Sulfate ($NiSO_4.6H_20$)	20.00 g/l
	Dimethylamine Borane Citric Acid	3.0 g/l
	Citric Acid	10.0 g/l
	Conc. HC1	25.0 ml/l
	Ammonium Hydroxide	to pH 7.0
	2-mercaptobenzothiazole	0.5-2.0 mg/l
	65°C.	
2.	Nickel Chloride ($NiCl_26H_20$)	16.0 g/l
	Dimethylamine Borane	3.0 g/l
	Sodium Citrate	18.0 g/l
	Glycine	8.0 g/l
	Bismuth Nitrate	20.0 mg/l
	Thiourea	15.0 mg/l
	pH 7.0, 65°C	

Nickel is deposited on the receptive surfaces by electroless deposition to form an electrically conductive nickel coated surface formed from a nickel-boron alloy rather than a nickel phosphorous alloy. Nickel ions are reduced in this process to nickel metal coated onto the catalytic surface of the monofilaments to form a completely and substantially uniform electrically conductive layer. A typical specific resistivity of a nickel-boron alloy is between about 8 and 15 micro-ohm cm. A typical specific resistivity of nickel-low phosphorous alloy is 20-50 micro-ohm cm; and for a nickel-high phosphorous alloy between 150-250 micro-ohm cm. The electroless layer is sufficiently thick to permit subsequent electrolytic deposition of a uniform metal layer such as copper. Generally, the electroless nickel layer is between about 0.1 and 1.0 micrometer thick but can be thicker if desired.

The nickel coated monofilaments can be further coated with electrolytic metal such as electrolytic copper in an electrolytic plating process step. In a preferred electrolytic plating process step, the nickel coated yarn is passed through an electrolytic plating bath under little or no tension so that the aqueous electrolytic plating bath can penetrate into the entire yarn to contact all nickel coated monofilament surfaces. An electrical charge is applied to the electrolytic plating bath to effect electrolytic metal deposition completely and substantially uniformly on all nickel surfaces. The thickness of the electrolytic metal coating can be controlled by controlling the time, temperature and metal concentration of the bath and by controlling the amount of electrical charge through the bath in a manner well known in this art.

The following examples illustrate the present invention and are not intended to limit the same.

EXAMPLE 1

Para-aramid yarn of 200 denier(d) with 89 monofilaments was treated for 90 seconds in an aqueous activating solution of 79% sulfuric acid which contained 50 ppm of a 3: 1 mixture of a perfluorinated alkyl ester surfactant and a perfluorinated alkyl alkoxylate surfactant at 40°C. The para-aramid yarn was a product sold by E. I. du Pont de Nemours and Company under the tradename "Kevlar". The yarn was then rinsed with water and conveyed through a continuous treating process under zero or very low tension on a carrier film as shown in the figure. The continuous process included a series of steps in a series of devices as shown in the figure with solutions which provided the catalyst system prior to electroless nickel deposition, final rinse, drying, and wind-up steps. The yarn first passed through a solution which was about 5% NaOH which rendered the monofilament surfaces alkaline prior to passing into a palladium activating solution which was an ionic soluble palladium complex sold by Atotech, Inc. under the trade name, Neoganth 834. This solution was made up by using 3% of the Neoganth 834 palladium activator concentrate in 96.5% by volume deionized water with 0.5% of 50% NaOH solution used to adjust the pH to 11.5. The bath was heated to 50°C for about 2 hours and was then cooled to 45°C for use in treating the yarn. Following the palladium bath, the yarn was passed through two rinse stations, each providing about 1 minute rinse with deionized water, then into a dimethylamineborane reducer solution sold by Atotech, Inc. under the tradename "Neoganth WA. The reducer solution was made by taking 0.5% by volume of the Neoganth WA concentrate and diluting it with 99% deionized water containing 0.5% boric acid as a pH buffer. This solution was heated to 35°C for use in reducing the soluble palladium ion to the palladium metal which provides active catalytic sites on the polymer surface to initiate electroless nickel deposition. The yarn was conveyed directly from the reducer solution into an electroless nickel plating bath comprising Niklad 752, available from MacDermid Corp. This bath was operated at 70°C with a pH of 6.6 and contained dimethylamine borane as the reducing agent; and was made up according to the supplier's instructions for the desired percent of nickel and reducer. The yarn was conveyed through the bath while supported on a carrier film under very low tension. Using high agitation in the bath, it was possible to obtain complete

penetration of the bath into the yarn bundle and uniform metalization of each monofilament. Typically, a 4 minute dwell time in this bath provided about 30% weight increase to the yarn by the nickel coating. The resultant coated yarn had a resistance of about 100 ohms/ft. Additional yarns processed with shorter dwell times provided proportionately less nickel and higher resistances, while longer dwell times provided proportionately higher metal addition with lower resistance. A cross-sectional analysis provided revealed complete and uniform deposition of nickel around all of the monofilaments in the yarn bundle.

EXAMPLE 2

A hollow picture frame type rack was cut out of 1/1 6" polyethylene sheeting and U-shaped grooves were milled on the top and bottom of the rack so that yarn could be wound around the rack loosely without tightly aggregating the monofilaments at the turnaround contact junctions on the side of the rack. About 20-25 ft. of the yarn treated by the acid surfactant activating solution of Example 1 were wound on a rack and hand dipped in the following process solutions in the following sequence: 2 minutes in a 5% NaOH pre-dip solution at ambient temperature and pH 11.5; direct immersion for about 2 minutes at 45°C in a palladium catalyst solution available from Atotech Corp as Activator 834; followed by a 1 minute rinse in deionized water: then immersion for 2 minutes in Neoganth WA reducer at 30-35°C followed by immersion into a low phosphorous electroless nickel bath. This bath was prepared by adding 190 milliliters of Niklad 797A (metal concentrate) and 570 milliliters Niklad 797B (sodium hypophosphite solution), both available from MacDermid Corp. and deionized water to make up 3.8 liters of electroless nickel plating solution. The pH was adjusted to 5.0-5.2 with 50% ammonia and the solution was heated to 90°C prior to immersion of the rack containing the yarn sample. The racks were agitated while being immersed for 5 minutes in the electroless nickel bath. This resulted in a 33% weight increase of the yarn due to the nickel coating. The final dried yarn had a resistance of 300 ohms/ft. which was three times higher than the coated yarn of Example 1.

EXAMPLES 3 AND 4

Examples 1 and 2 were repeated except that the yarns were treated in concentrated sulfuric acid for a much shorter time as taught in U.S. Patent 5,302,415. To minimize substantial degradation of the monofilaments. it was

necessary to limit the immersion of the yarns in the concentrated sulfuric acid to only half as long as the immersions of Examples 1 and 2. The coated yarns exhibited electrical resistances similar to the coated yarns of Examples 1 and 2.

EXAMPLE 5

The metalized yarn obtained by the process of Example 1 was subsequently electroplated with copper by passing the nickel coated yarn through a gas agitated electrolytic acid copper sulfate plating bath fitted with contact bars which passed electrical current into the yarn as it entered and exited from the plating bath. The nickel coated yarn could withstand about 5 amps of current before sustaining yarn damage and added about 65% by weight of copper to produce a material that had a resistance less than 1 ohm/ft. This copper plated yarn still retained all of the good handling, drape, and flexibility characteristics of the original starting yarn. This electrolytic plating provided a fine grained equi-axial crystal structure on the copper.

WHAT IS CLAIMED IS:

1. A process for modifying the surface of a polymeric monofilament to render said surface water-wettable characterized by contacting said surface with an aqueous activating solution comprising sulfuric acid or a strong acid derivative of sulfuric acid having a concentration of 75 to 85 percent by weight and a surfactant for a time period and temperature sufficient to render said surfaces water-wettable but less than that wherein substantial mechanical degradation of said monofilament occurs.

2. The process of Claim 1 wherein said acid is sulfuric acid.

3. The process of Claim 1 wherein said surfactant is fluorinated surfactant.

4. The process of Claim 1 wherein the surfactant is an amine perfluorosulfonate.

5. The process of claim 1 wherein the surfactant is a fluorinated alkyl alkoxylate.

6. The process of claim 1 wherein the surfactant is a fluorinated alkyl alkoxylate ester.

7. The process of claim 1 wherein the surfactant is a fluorinated alkyl alkoxylate salt.

8. The process Claim 1 wherein said polymeric surface is formed from aramid.

9. The process of Claim 1 wherein said polymeric surface is formed from polyamide.

10. The process of Claim 1 wherein said polymeric surface is formed from polyester.

11. A process for completely and substantially uniformly coating the surface of a polymeric monofilament with an electrically conductive electroless nickel coating wherein said surface is modified by the process of claim 1 prior to coating with said nickel characterized by feeding said monofilament from at least one feed reel, through an electroless nickel bath to at least one take-up reel wherein tension on said monofilament within said bath is sufficiently low to permit complete and substantially uniform coating.

12. The process of Claim 11 including the additional step of coating said electroless nickel coating with at least one electrolytic metal.

13. The process of Claim 12 wherein said electrolytic metal coating is electrolytic copper.

14.The process of Claim 12 wherein said electrolytic metal coating is electrolytic nickel.

15. A polymeric monofilament completely and substantially uniformly coated with an electrically conductive electroless nickel-boron alloy coating.

16. The monofilament of claim 15 wherein said monofilament is solid.

17. The monofilament of claim 15 wherein said monofilament is hollow.

18. The monofilament of Claim 15wherein said monofilament is formed from aramid

19. The monofilament of Claim 15wherein said monofilament is formed from polyamide.

20. The monofilament of Claim 15wherein said monofilament is formed from polyester.

21. The monofilament of Claim 15 wherein said nickel-boron alloy coating is further coated with at least one electrolytic metal.

22. A yarn formed of a multiplicity of the monofilaments of Claim 15.

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